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Effect of Dextrin and Thiourea Additives on the Zinc Electroplated Mild Steel in Acid Chloride Solution

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The performance effects of thiourea and dextrin as addition agents on the electroplating of zinc on mild steel in acid chloride solution were experimentally investigated. The experiments were performed under different additive concentrations, different plating time and fixed pH conditions. The zinc electroplating on mild steel was performed using a DC – supply at defined operating parameters. The surface of the plated steel was examined using scanning electron microscopy (SEM) for surface morphology; and Energy Dispersive Spectroscopy (EDS) for surface elemental composition analysis. Different surface characteristics were obtained depending upon the concentration of the additive and the plating time. The corrosion resistance of the plated surface was determined by gravimetric method. The quality of the electro-deposition of zinc was good as indicated by the microstructural feature of the plated surface. The electrodeposition process was sensitive to changes in additive concentration and plating time. Variations in the plating parameters produced entirely new and different surface morphology.

Keywords: Electroplating, dextrin, thiourea, steel surface, acid chloride solution, corrosion,

1. INTRODUCTION

In spite of the availability of the commercially-available proprietary additives [1-4] that have been in use for some years, the need to improve on these and to develop other non-commercial proprietary additives for the acid chloride bath has been considered to be of necessity . This has also generated increased research interest including the present investigation. The growing interest in this field of electrodeposition research has also been necessitated by the need to prevent corrosion and toxicity and to enhance the aesthetic value of steel components in different manufacturing productions, industries and services facilities and in our daily lives adds. This work is also a further contribution to

the recent investigations [5-9] which characterized the surface effects of additives on the electrodeposition of zinc on mild steel in acid-chloride solution under different conditions. Many other authors [10-13] have also reported in different areas of zinc and zinc alloys electrodeposition and on synergistic effect of electrodeposited alloys/ effect of addition agents and also on their corrosion resistance characteristics using different bath solutions.

Chloride zinc solution does not only eliminate cyanide in plating, it also gives improved bath efficiency and exceptional brightness. And zinc baths are used where it is desirable to have a high plating rate and low cost. Chloride zinc plating offers considerable advantages over cyanide-based systems, although it is not without its share of routine operating problems [3]. Use of the acid sulphate process is increasing due to its relatively low cost, safety features and pollution control characteristics, but throwing power and insufficient brightness from an acid sulphate bath are disadvantages [9].

In most studies, major interest is given to the development and exploration of new substances to be used as brighteners for the electroplating process to generate smooth and levelled bright deposit capable of providing higher corrosion resistance [14]

Usually, the electroplating baths are associated with two or more addition agents and are essential to obtain a quality deposit [15]. However, too many ingredients cause difficulties in maintaining the operating parameters of the bath solution during the plating process. Therefore, it is essential to develop the bath with a single additive that could produce a quality deposit [16]. The importance of additives in electroplating solutions, acidic and alkaline but especially in acidic ones, cannot be over emphasized. The primary goal of all these baths is to generate quality zinc deposit with good corrosion protection ability to steel. The corrosion resistant property of zinc deposit depends mainly on its fine grained nature, smoothness, levelling and degree of brightness.

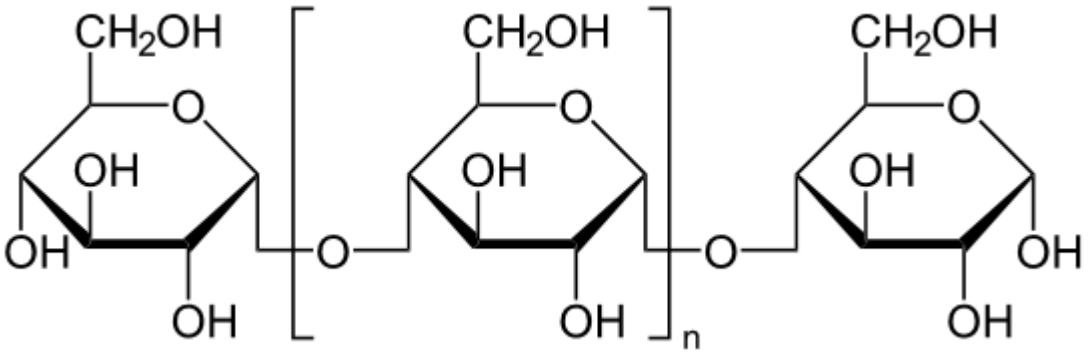
The additives used in electroplating are classified as primary and secondary which always in combination produce bright deposit on an initially dull substrate or which maintains brightness on an initially bright coating. Most of the primary additives are surfactants (wetting agents, levellers and grain refiners) whereas secondary additives [brighteners] are organic compounds like aromatic and aliphatic aldehydes, ketones, sulphur containing compounds, and alkyl aryl ammonium salts. The primary additives add levelling and smoothness to the deposit while secondary additives add brightness. Secondary additives include benzylideneacetone [17] and vanillin [18]. The focus of this research work aims at imparting brightness, levelling, grain- refinement and corrosion resistance to the plated surface with the use of the organic chemicals to enhance the plating quality. It is envisaged that the use of dextrin and thiourea will achieve these objectives.

2. MATERIALS AND METHODS

The additives

Thiourea was obtained in liquid state and hence did not need to be dissolved in order to be used. Dextrin on the other hand was obtained in powder form. The dextrin additive was added in liquid phase to the electroplating solution. This additive was prepared by dissolving 10g of dextrin powder in 10ml of distilled water.

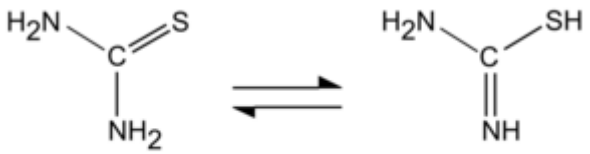
Dextrins are a group of low-molecular-weight carbohydrates produced by the hydrolysis of starch [19] or glycogen [20]. Dextrins are mixtures of polymers of D-glucose units linked by α-(1→4) or α-(1→6) glycosidic bonds.



Dextrin molecular structure

Dextrin can be produced from starch using enzymes like amylases, as during digestion in the human body and during malting and mashing,[21] or by applying dry heat under acidic conditions (pyrolysis or roasting). The latter process is used industrially, and also occurs on the surface of bread during the baking process, contributing to flavour, colour, and crispness. Dextrin produced by heat is also known as pyrodextrin. Dextrin is usually defined as a soluble gummy substance, formed from starch by the action of heat, acids, or ferments, having dextrorotatory properties: used chiefly as a thickening agent, as mucilage and as a substitute for gum Arabic and other natural substances.

Thiourea, also called thiocarbamide, is an organosulphur compound with the formula $SC(NH_2)_2$ or CH4N2S. It is structurally similar to urea, except that the oxygen atom is replaced by a sulphur atom, but the properties of urea and thiourea differ significantly. Thiourea, a reagent in organic synthesis, is a planar molecule. The C=S bond distance is 1.60±0.1 Å for thiourea (as well as many of its derivatives). The material has the unusual property of changing to ammonium thiocyanate upon heating above 130°C. Upon cooling, the ammonium salt converts back to thiourea. Thiourea occurs in two tautomeric forms. In aqueous solution, the thione shown on the left below predominates:



Thione form Thiol form

2.1 Experimental set-up

The experimental set-up and further procedures followed some of the similar previous studies [5-7]. Flat mild steel, SIS 14147, 0.1 cm thick, with a nominal composition of 0.038% C, 0.195 Mn

and the remainder Fe, was cut into several test specimens of 10.0 cm long and 1.0cm wide. A portion of 1.0 cm in length was marked off at one end for the electroplating of zinc. The test specimens were degreased ultrasonically for 5 minutes with an alkaline degreasing chemical and then removed from the solution, rinsed in distilled water, immersed in methanol, and air dried. The specimens were, in turns, etched for 50 seconds in 3M HCl, rinsed in distilled water, immersed in methanol, air dried and stored in a desiccator for further experimental process.

The acid chloride solution for the electrodeposition consisted of ZnCl (71g/l), KCl (207g/l) and H_3BO_4 (35g/l). Thiourea, dextrin and their combinations of varying concentrations /50ml of acid chloride solution were used in turns as the addition agents (Table 1).

Table 1. The bath addition agent and concentration used

Additives	Quantity/50 ml of acid chloride	Concentration %
Dextrin	a. 2.0ml	4
	b. 4.0ml	8
Thiourea	c. 4.0ml	8
	d. 2.0ml	4
	e. 1.0ml	2
Dextrin + Thiourea	f. 2.0ml	4
	g. 2.5ml	5
	h. 3.0ml	6

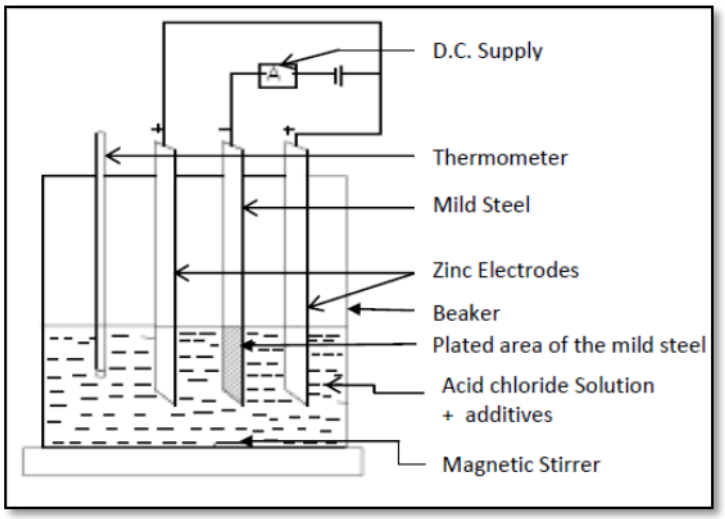


Figure 1. Schematic diagram of the experimental set-up

Electrodeposition of zinc on steel was performed by partially immersing the steel specimen and the zinc electrodes in the plating solution (20mm deep) through the rectangular hole made on a prepared plastic cover for the 250ml beaker used as the plating bath. The steel specimen was connected to the negative side of a DC supplier while the zinc electrodes were also connected with a wire to the

positive side, Fig. 1. In turns, the plating solutions were put into the beaker and their respective pH was obtained by adjusting the original solution with potassium hydroxide. The plating times used for each bath were mainly15 and sometimes, 18minutes. The weight of each steel specimen was taken before and after the electroplating process in order to determine the weight of zinc deposit by finding the difference between both weight readings, (Table 2).

Table 2. Mass of zinc deposited on steel substrate during plating

Sample	Mass Deposited(g)
2B	0.0252
3B	0.0211
4B	0.0193
5B	0.0103
9A	0.026
10B	0.0338
11A	0.0255
12B	0.0382
13B	0.024

The plating solution was stirred gently while the plating process was on to ensure even plating. The other operating conditions were: pH of the solution, 5; temperature, 27-30^{o}C; current 0.08A; Voltage, 13V DC; plating time, 15 and 18 min. After each plating experiment, the specimen was taken out, rinsed in distilled water, immersed in methanol, and quickly air-dried. The specimens were stored in a desiccator for further analysis of surface morphology and the electroplated zinc.

2.2. SEM/EDS characterisation

The examination of the surface morphology of each of the plated test specimens was done with a scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS). A small portion of each of the specimens was cut and mounted on a stub. The specimens were examined in turn in the SEM, and electron micrographs were made of the representative areas of the surface at different magnifications. Determination of the surface composition of the plated metal was done using the EDS.

2.3. Adhesion test

The adhesion of the zinc coating to the steel substrate was tested by using cellotape fastened to the surface and later pulled off. This was then visually observed for any zinc stripping from the plated steel's surface. The plated surface was further scratched with a scalpel to test for the zinc adhesion. The specimens were too small for a bending test.

2.4. Corrosion resistance testing of electroplated specimen

Corrosion resistance of the electroplated mild steel was tested gravimetrically. Each of the plated mild steel test specimens was partially immersed in the seawater test environment. The seawater was topped up to replace the amount lost due to evaporation. Weight Loss measurements were taken every two days for a period of 24 days. Corresponding corrosion rates values were determined from these weight loss values by calculation using this formula:

C.R. = 87.6W/DAT ….. (1)

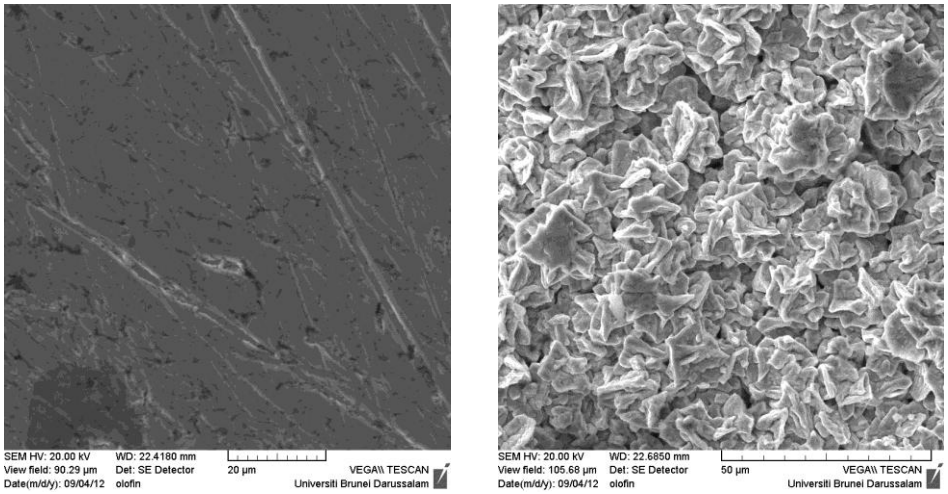
Where W is the weight loss in milligrams; D = the density in g/cm^2; A= the area in cm^2, and T = the time of exposure in hours. C.R. = Corrosion rate

3. RESULTS AND DISCUSSION

3.1. Electrodeposition of zinc

No addition of additives

The SEM micrograph of the surface of the mild steel test samples before zinc electro-deposition is presented in Fig. 2(i). Similarly, Fig. 2(ii) shows the micrograph of the zinc plated mild steel without the use of any additive. Electro-deposition of zinc on mild steel test samples from acid–chloride solution without any additive showed no apparent porosity at the portion photographed with the SEM. The crystals were distinct and closely packed but difficult to describe in shape. Coarse and fine particles could be seen to intersperse each.



(i) Sample not plated (ii) Plated without additive

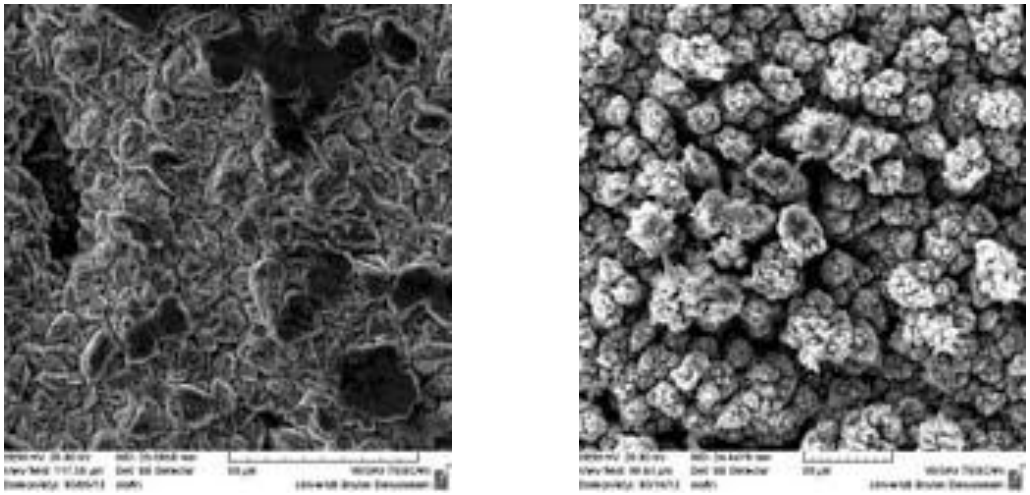
Figure 2. SEM micrographs of mild steel test sample: (i) sample not plated (ii) plated not with additives.

The surface crystals feature was not particularly smooth. The crystals were very much different from those plated with additives as will be observed below. The coarse structure could be due to the

absence of levelling agents in the acid solution. The viability of this type of zinc plating will certainly depend on the conditions under which the experiments are performed. The observed coarse crystal morphological structure of the plated sample surface could be associated with the poor throwing power of the acid solution.

Dextrin additive

The representative micrographs made for the zinc electroplating on mild steel at the same concentration of 4ml/50ml of acid chloride solution but at the different plating time of 15 and 18 minutes respectively are presented in Figure in 3.



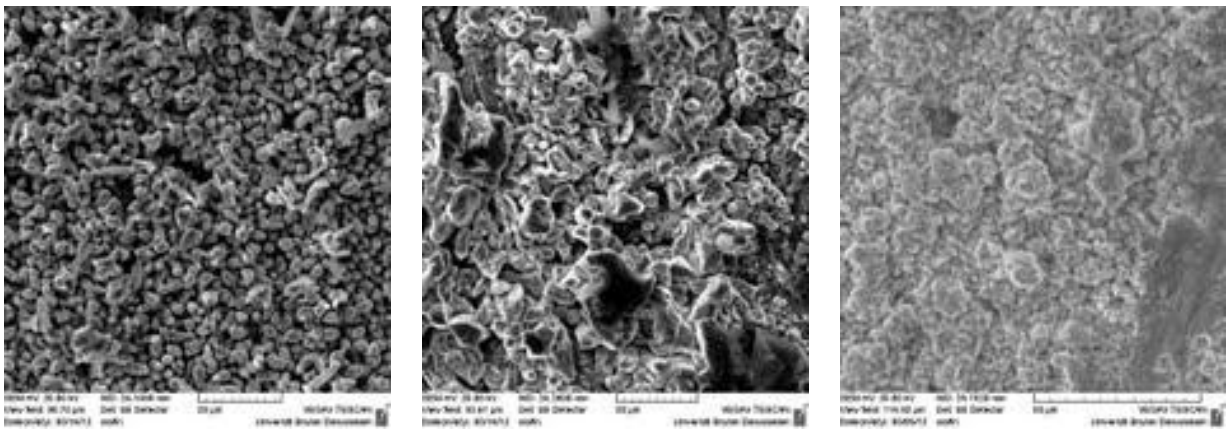
(i) 4ml at 15mins (ii) 4ml at 18mins

Figure 3. SEM micrographs of steel surface after zinc plating with 4ml /50ml of acid- chloride solution at (i) 15 and (ii) 18 minutes respectively.

Figure 3 (i) shows the surface microstructure to be more of fine grains, levelled and looks less bright. At the portions examined, there was no discernible porosity observed. The crystal particles were very close-packed and creating a well-defined surface microstructure. When compared with the Fig. 2 (ii), that is, with the one without added juice, a significantly clear difference in surface structure could be observed. Figure 3 (ii) in which the plating time was more (18 minutes) than the former, a completely different surface microstructure could be seen. The grains are very fine but seem to be closely packed in clusters and are brighter than in Figure 3 (i) for 15 minutes plating time. The distinct difference in surface structure here is due to the plating time effect. It is also clear that the observed fine grains and levelling difference in surface morphology as evidenced in Fig. 3(i-ii), emanated from the use of the dextrin additive. The difference in surface morphology in Figures 3 (i) and (ii) is significant. The unique microstructure observed in Fig.3 (i-ii), is evidence of good zinc electro-deposition. A densely packed surface structure, such as obtained here, is expected to give appreciable corrosion resistance performance [22-24]. The mass of zinc deposited was weighed to be 26 and 33.8 mg for 15 and 18 minutes plating time respectively, Table 2.

Thiourea additive

Presented in Figure 4 (i-iii) are the micrographs made for the zinc electroplating on mild steel in the acid chloride solution at the same plating time of 15 minutes but with different concentrations of additives of 4, 2 and 1ml/50 ml of acid chloride solution respectively.



(i) 4ml at 15mins (ii) 2ml at 15mins (iii) 1 ml at 15 mins

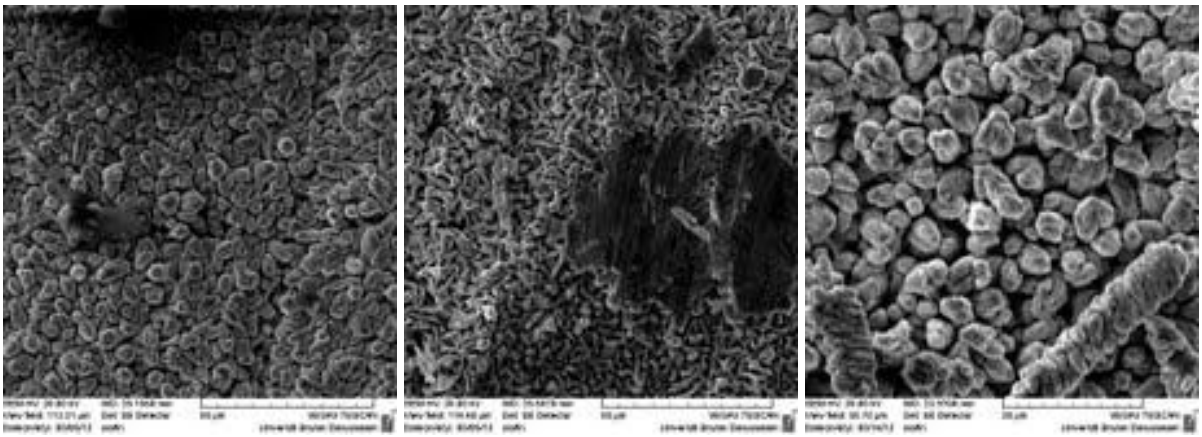
Figure 4. SEM micrographs of steel surface after zinc plating at 15 minutes plating time and at different concentrations.

The effect of variation in the additive concentration is very apparent with the different surface morphology obtained. Figure 4 (i), the plating with 4 ml/50ml acid chloride solution presents very fine granular microstructure, well levelled and closed pack microstructure with good brightness. With the use of 2ml/50ml acid chloride solution, Figure 4 (ii), the surface microstructure looks different from the former morphologically. No distinct granular shape is obtained here; however, the surface was levelled, close packed and bright. Figure 4 (iii) with 1 ml/50mlacid chloride solution gave a fairly dull electroplating with surface microstructure that is different from the other two just described. The surface structure also is closed packed and fairly levelled. In all, there is no porosity observed. The use of thiourea in electroplating as an additive can therefore be described as giving good surface plating quality but the higher the concentration of the additive within the quantity used the better the plating. The mass of zinc deposited on each of the test samples above was 25.2, 21.1 and 19.3 mg respectively for the 4, 2, and 1 ml/50ml acid chloride solution. It is expected that the plating will sacrificially and cathodically exhibit good corrosion protection.

Combination of Dextrin and Thiourea

The combination of dextrin and thiourea looks at both the concentration and plating time effect synergistically. The micrographs obtained from the electroplating of zinc on mild steel in acid chloride solution using the different concentration and plating time of the combined additives are presented in Figure 5 (i-iii) respectively. The crystal grains on the surface vary with the changing additive concentration. A bright zinc deposition was achieved in each of the plated samples. There was no

porosity observed within the micrographs. The surface morphology show very compact, levelled, fine and in some cases roundish crystals. All these are indications of very good quality zinc electro-deposited surface microstructure. A good corrosion protection performance is expected in this regard. It is clear that both the concentration of the additive and the plating time are important factors in achieving good zinc plating in acid chloride solution.



(i) 4ml at 15mins (ii) 4ml at 18mins (iii) 6ml at 15mins

Figure 5. SEM micrographs of steel surface after zinc plating at different plating time and different concentrations of combined dextrin and thiourea additives.

EDS Analysis

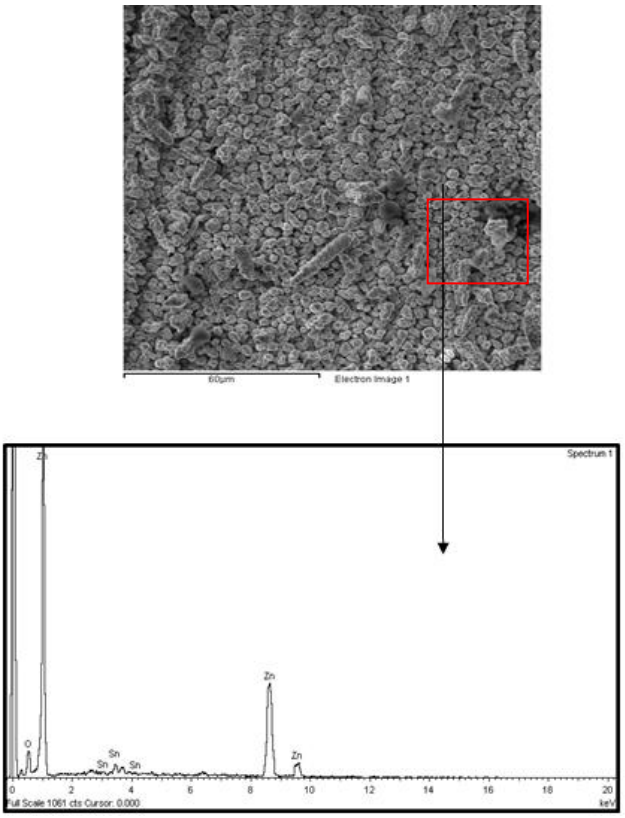


Figure 6. EDS analysis of the plated surface of sample in Fig.3 (ii)

The result of energy dispersive analysis (EDS) of Fig. 3 (iii) is presented in Fig. 6. The surface microstructure showed it to be mainly zinc and a little amount of tin which could be in trace form in the zinc metal that was co-deposited.

3.2. Corrosion resistance of the zinc plated mild steel

Results of the weight- loss method and the calculated corresponding corrosion rates of the zinc plated mild steel samples, using dextrin and thiourea additives and in combination, that were tested in the sea water medium are presented in Figures 7 to 16.

Dextrin additive

Figure 7 shows the curves of the weight loss versus the exposure time at different concentrations of dextrin additive and at the plating time of 15 minutes for each of the test samples.

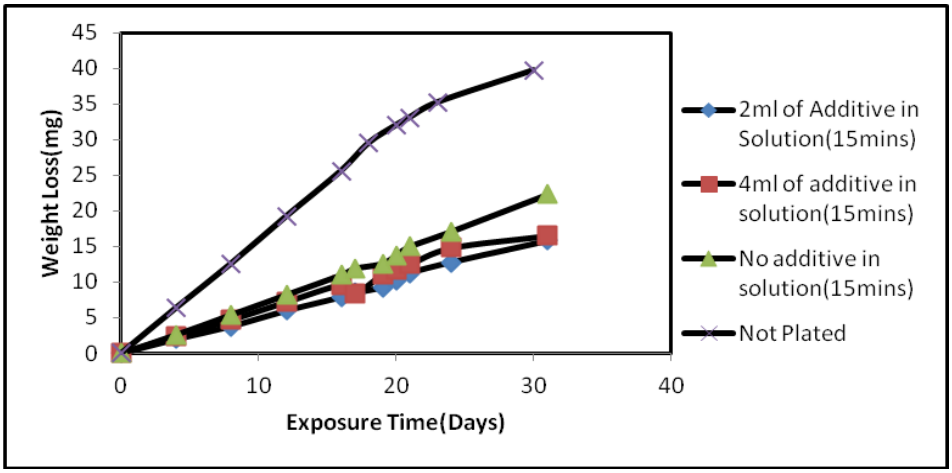


Figure 7. Variation of weight loss with exposure time for the zinc electrodeposited mild steel - sample in seawater. (Variable dextrin additive concentrations and 15 minutes plating time)

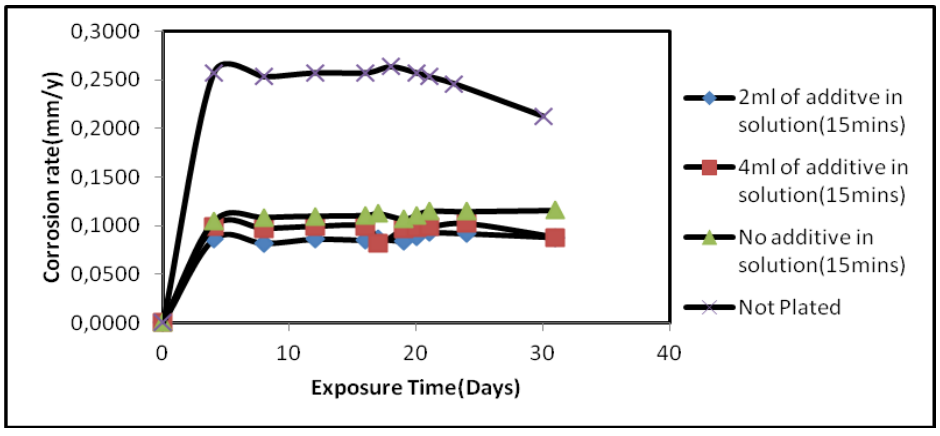


Figure 8. Variation of corrosion rate with exposure time for the zinc plated mild steel samples in seawater. (Variable dextrin additive concentrations and 15 minutes plating time)

All the plated samples showed better corrosion resistance than the unplated samples.While the unplated sample recorded a weight loss of 39.70 mg on the 30th day of the experiment, the samples plated with 2 and 4ml dextrin /50 ml acid chloride solution respectively recorded a weight loss value of 16.50 mg at the same period of 30 days of the experiment. The weight loss recorded for the plated samples was due mainly to the anodic zinc dissolution in the test environment after a long period of 30 days.

The corresponding corrosion rates curves are presented in Fig.8. The unplated test sample recorded the highest corrosion rate starting from the 4th day (0.2572mm/yr) and achieving the highest corrosion rate on the 18th day (0.2635 mm/yr) of the experiment respectivel. On the 30th day, the last day of the experiment, the corrosion rate value recorded was 0.2127 mm/yr. The sample plated with 2 and 4 ml dextrin /50ml acid chloride solution respectively, recorded the corrosion rates of 0.1109 and 0.0881 mm/yr on the 20th day and and 30th day of the experiment respectively. These corrosion rate values are much lower than the one recorded for the unplated metal sample in the same test environment. The plated sample without additive also gave a better corrosion resistance though less than the values of corrosion rates achieved for the samples with the use of dextrin additive. The grain refinning and levelling action of the additive had modified the surface microstructure and hence better surface morphology and better corrosion resistance. The zinc plating, in fact, under went anodic dissolution and sacrificially protected the mild steel substrate. This phenomenon accounted for the weight loss and corrosion rate values recorded during the experiments.

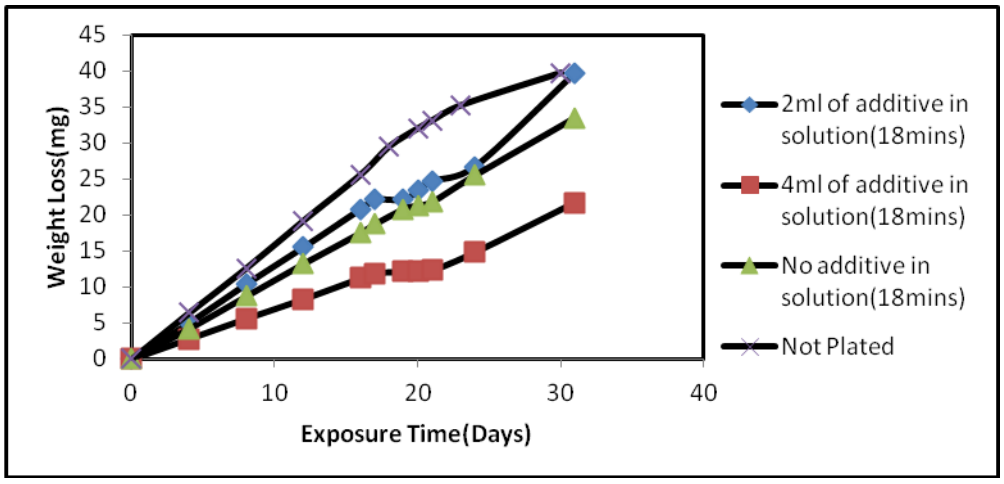


Figure 9. Variation of weight loss with exposure time for the zinc plated mild steel samples in seawater. (Variable dextrin additive concentrations and 18 minutes plating time)

The results presented in the curves in Figs. 9 (weight loss) and Fig.10 (corrosion rates) were obtained with the plating time of 18 minutes using dextrin as the addition agent. Just as in Fig.7, the trend of corrosion resistance for the weight loss values looked similar. All the plated (with and without the additive) gave better corrosion resistance performance than the unplated samples. The samples plated with 4ml dextrin additive, gave the lowest weight loss throughout the experimental period, achieving the weight loss values of 12.2 and 21.7 mg on the 20th and 30th day of the experiment

respectively.The same additive concentration recorded the lowest corrosion rate (Fig. 10) values of 0.0861 and 0.0989 mm/yr on the 20th and the 30th day of the experiment respectively. The results obtained here shows that the higher concentration of the dextrin additive used gave better plating quality and hence better corrosion resistance. The higher concentration of the additive also gave appreciable mass of zinc (26mg) deposited on the mild steel substrate.

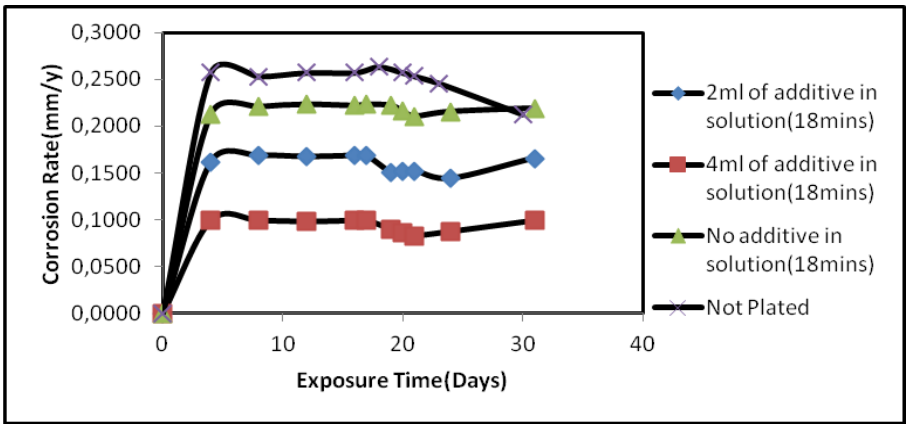


Figure 10. Variation of corrosion rate with exposure time for the zinc plated mild steel samples in seawater. (Variable dextrin additive concentrations and 18 minutes plating time)

Thiourea additive

The corrosion resistance results obtained for the plating done with thiourea as the additive in the acid chloride solution are presented in Figs. 11 and 12 for the weight loss and corrosion rates respectively. In Fig. 11, the same trend as in Fig. 7 could be observed. All the variable concentrations had lower weight loss values than the mild steel sample not plated. The lowest weight loss value (22.3 mg) was, however, achieved with the plating with 4ml/50ml acid chloride solution on the last day of the experiment.

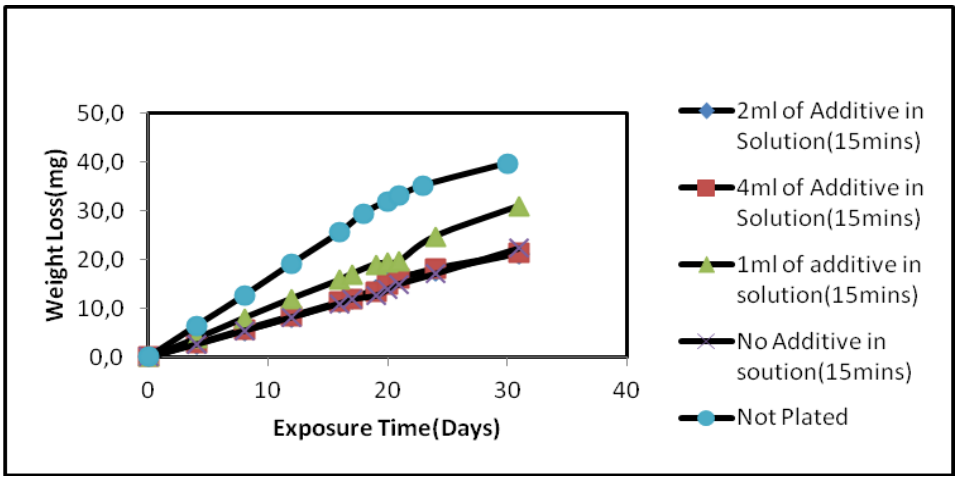


Figure 11. Variation of weight loss with exposure time for the zinc electrodeposited mild steel - sample in seawater. (Variable thiourea additive concentrations and 15 minutes plating time)

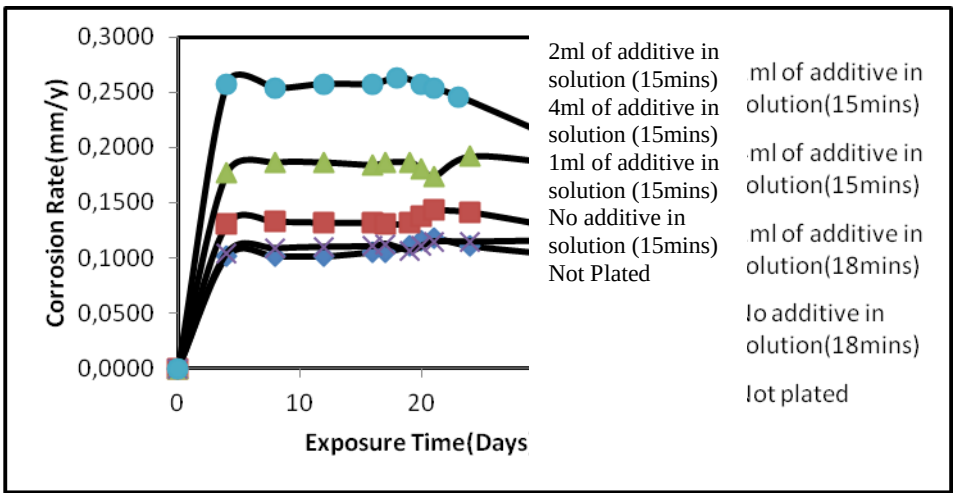


Figure 12. Variation of corrosion rate with exposure time for the zinc plated mild steel samples in seawater. (Variable thiourea additive concentrations and 15 minutes plating time)

The corresponding corrosion rate curves presented in Fig. 12, also confirmed all the samples plated with thiourea additive had very much lower corrosion rate values (0.1028 and 0.1156 mm/yr – the lowest values) than the metal sample that was not plated (0.2127 mm/yr). These results and the above are clearly in agreement with similar previous studies [22-24].

Synergism of dextrin and thiourea additives

The results obtained for corrosion resistance of the plated samples using the combination of dextrin and thiourea at two different plating time (15 and 18 minutes) and variable concentrations are presented in Figs. 13 to 16. Figs. 13 and 14 showed the weight loss and the corresponding corrosion rates curves respectively for the plating time of 15 minutes.

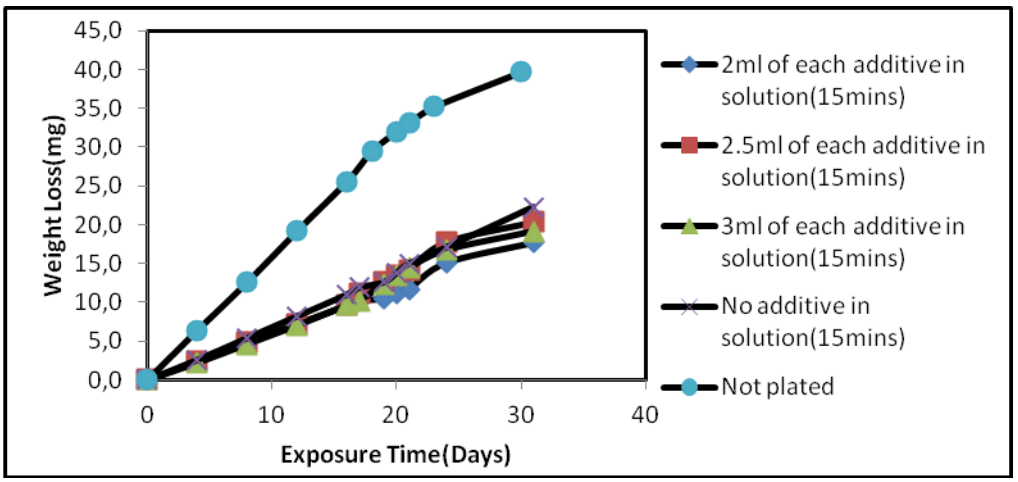


Figure 13. Variation of weight loss with exposure time for the zinc plated mild steel sample in seawater. (Variable dextrin + thiourea additive concentrations at 15 minutes plating time)

The weight loss values for the zinc plated samples with and without additives (17.7 – 22.3mg) are much lower than the weight loss values of sample not plated (39.7mg) as at the last day of the experiment. Similarly, the corrosion rate values in Fig. 14 had values (0.0820 and 0.1156 mm/yr) much lower than the unplated sample (0.2127 mm/yr) as at the last day of the experiment.

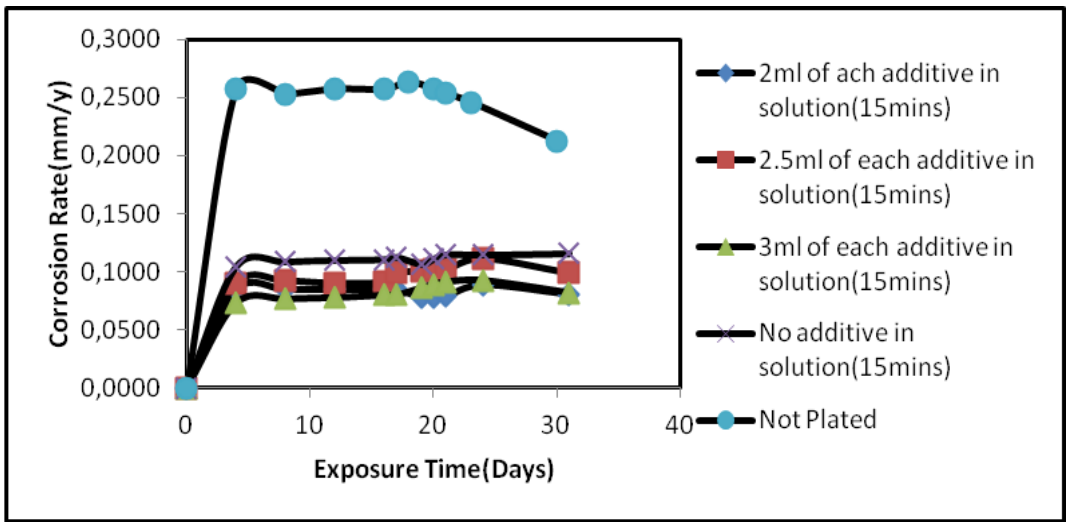


Figure 14. Variation of corrosion rate with exposure time for the zinc plated mild steel sample in seawater. (Variable dextrin + thiourea additive concentrations at 15 minutes plating time)

The corrosion resistant performance of these combined additives at the 15 minutes plating time, are not much better than the use of individual additives. The plated zinc undergo the same anodic dissolution to sacrificially protect the mild steel.

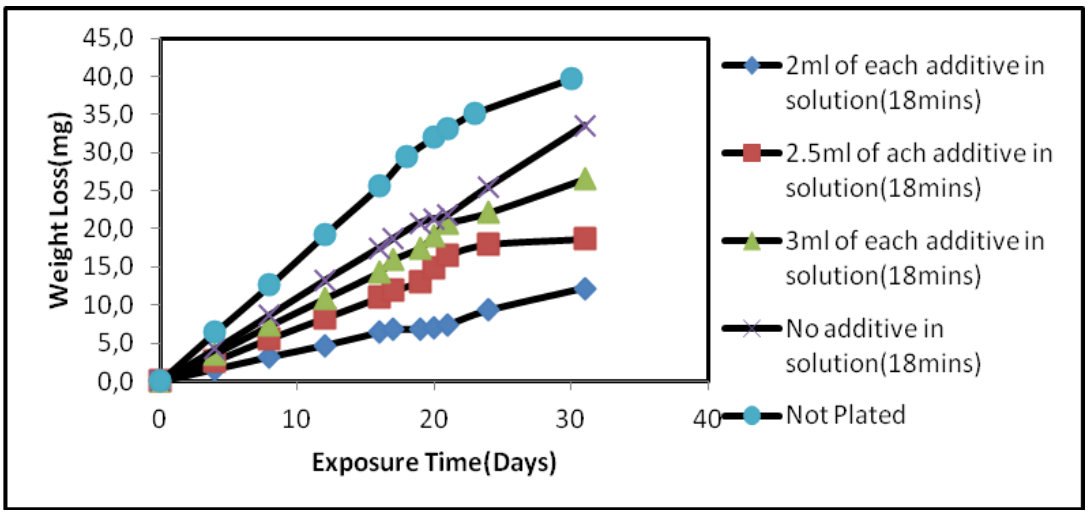


Figure 15. Variation of weight loss with exposure time for the zinc plated mild steel sample in seawater. (Variable dextrin + thiourea additive concentrations at 18 minutes plating time)

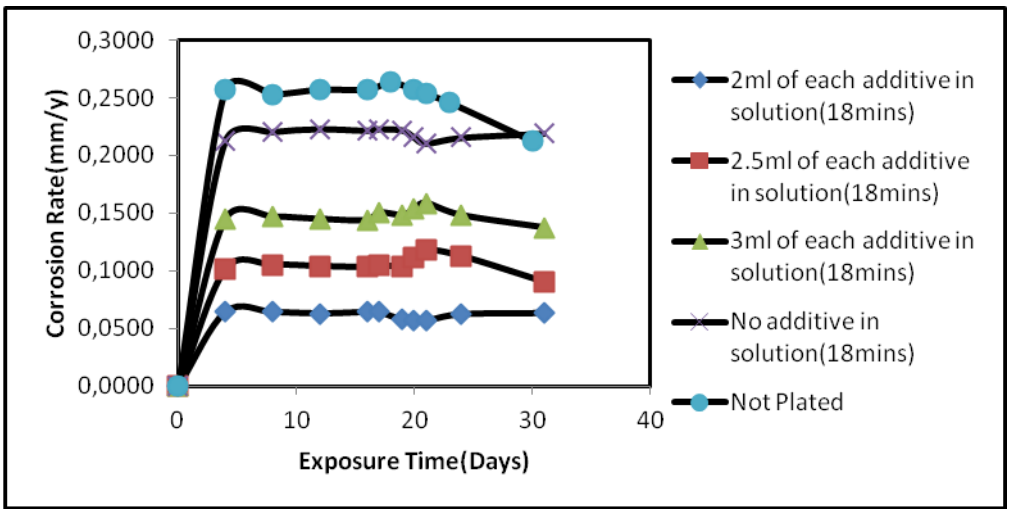


Figure 16. Variation of corrosion rate with exposure time for the zinc plated mild steel sample in seawater. (Variable dextrin + thiourea additive concentrations at 18 minutes plating time)

Figs. 15 and 16 showed the weight loss and the corresponding corrosion rates curves respectively for the plating time of 18 minutes. The weight loss values for the zinc plated samples additives ranged from 12.2, 18.7, and 26.5 mg for 2, 2.5, 3 ml combined additive/50ml acid chloride solution respectively. The sample without additive recorded a weight loss value of 33.5 mg at the same period of the experiment. All these values are much lower than the weight loss values of the sample not plated (39.7mg) as at the last day of the experiment.

These results do not only confirm the effectiveness of zinc depostion on the mild steel substrate with respect to corrosion protection, but also confirmed the effect of the synergism of the combined additives on the plated surface morphology.

The corrosion rate values as presented in Fig. 16 show results of low corrosion rate, which mainly will be due to the plated zinc dissolution to sacrificially protect the mild steel substrate as earlier mentioned. The various combined dextrin and thiourea additive concentrations gave different corrosion rates that range from 0.0633, 0.0907 to 0.1374 mmm/yr for the 2, 2.5 and 3ml / 50ml acid chloride solution respectively. The plating without additive recorded a corrosion rate of 0.2192mm/yr while the sample not plated had a corrosion rate of 0.2460 on the 23rd and 0.2127 mm/yr on the last day of the experiment. These results also confirmed effectiveness of the combined additive on the quality of the zinc electroplated surface. It is important to mention here, that the plating at 18 minutes using the combined additives gave better, that is, lower corrosion rates values comparatively.

In all, as could be seen in the results as contained in the curves, the plated samples were more corrosion resistant and hence more protective. Again this is due to deposited zinc going into dissolution to sacrificially protect the mild steel substrate. Also from the results, it could be inferred that the rate/ magnitude of zinc dissolution is minimal.

It is also important to mention that the results obtained for corrosion resistance performance of the samples bear very close correlation with the surface microstructure in the micrographs and also to the mass of zinc electrodeposited on the plated portions. The more compact the surface crystal particles; the finer the crystal structure and the more the corrosion resistance observed.

The cellotape test confirmed the strong adhesion of the zinc to the steel surface. Visual inspection could not reveal any visible particle removed from the plated steel surface. Apparently, a good zinc plating was achieved with the use of the dextrin and thiourea additives within all the plating conditions/parameters used.

4. CONCLUSIONS

1. Using dextrin and thiourea as the addition agents` gave good zinc electrodeposition with fine, dense and close- packed crystal grains on mild steel surface in the acid zinc chloride solution. There was no porosity observed on the zinc plated surface of the mild steel.
2. Characterisation of the zinc plated surface of the mild steel substrate showed different surface morphology depending upon the plating conditions.
3. The dextrin and thiourea additives gave very significant levelling and grain-refinement of the deposited zinc on the mild steel substrate when separately used and when used in combination. The fine and roundish structure showed good quality electroplating of zinc on the substrate.
4. The electrodeposition process was sensitive to changes in additive concentration and plating time. Any variation in the plating parameter produced an entirely new and different surface crystal strucure.
5. The plated samples showed good corrosion resistance in seawater test when compared with the unplated samples and thus confirming their expected protective capability.
6. The plating produced bright deposition and the good levelling showed the good throwing power of the acid bath.

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